

Interplay of octahedral rotations and breathing distortions in charge ordering perovskite oxides

Prasanna V. Balachandran and James M. Rondinelli*

Department of Materials Science & Engineering, Drexel University, Philadelphia, PA 19104, USA

(Dated: March 6, 2013)

We investigate the structure–property relationships in ABO_3 perovskites exhibiting octahedral rotations and cooperative octahedral breathing distortions (CBD) using group theoretical methods. Rotations of octahedra are ubiquitous in the perovskite family, while the appearance of breathing distortions – oxygen displacement patterns that lead to approximately uniform dilation and contraction of the BO_6 octahedra – are rarer in compositions with a single, chemically unique B -site. The presence of a CBD relies on electronic instabilities of the B -site cations, either orbital degeneracies or valence-state fluctuations, and often appear concomitant with charge order metal–insulator transitions or B -site cation ordering. We enumerate the structural variants obtained from rotational and breathing lattice modes and formulate a general Landau functional describing their interaction. We use this information and combine it with statistical correlation techniques to evaluate the role of atomic scale distortions on the critical temperatures in representative charge ordering nickelate and bismuthate perovskites. Our results provide new microscopic insights into the underlying structure–property interactions across electronic and magnetic phase boundaries, suggesting plausible routes to tailor the behavior of functional oxides by design.

PACS numbers: 61.50.Ks, 31.15.xh, 71.30.+h

I. INTRODUCTION

Perovskite oxides with chemical formula ABO_3 and B -site transition metal (TM) cations exhibit a range of functional electronic transitions that are intimately tied to the structure of the fundamental building blocks:¹ (i) the site-symmetry of the BO_6 octahedron defined by the B –O bond lengths, and (ii) the tilting of corner-connected octahedra. Adjacent BO_6 units typically fill space in perovskites through nearly rigid rotations, which produce deviations of the B –O– B bond angles away from the ideal 180° found in the cubic aristotype ($Pm\bar{3}m$ symmetry); the rotations are described by two three-dimensional irreducible representations (irreps), M_3^+ and R_4^+ , of the high-symmetry structure.² Combinations of these lattice instabilities – cooperative bond length distortions and octahedral rotations – interact across *structural* phase transitions through elastic stresses and symmetry allowed coupling invariants as described within Landau theory.

Beyond changes to crystallography, the transition from high temperature (high symmetry) to low temperature (low-symmetry) can also produce *electronic* metal–insulator (MI) transitions. Perovskite oxides with B -site cations in $t_{2g}^3 e_g^1$ (d^4), $t_{2g}^6 e_g^1$ (d^7) and $t_{2g}^6 e_g^3$ (d^9) electronic configurations are particularly susceptible, because the low-energy electronic structure is dictated by the octahedral crystal-field split antibonding e_g orbitals—the atomic-like d -states that are spatially directed at the coordinating oxygen ligands. MI-transitions which occur simultaneously with lattice distortions are common in low-dimensional materials, e.g. Peierls systems.³ In three-dimensional perovskite oxides, however, the most familiar electronic transitions with concomitant changes in the B –O bond lengths and octahedral rotations result from cooperative first-order Jahn-Teller effects: Tetrag-

onal elongations of the BO_6 octahedra occur to remedy the orbital degeneracies that *localized* electrons encounter for particular B -site cation configurations. And through these distortions, the crystal maintains a uniform TM valence among all B -sites across the transition.⁴ The Jahn-Teller distortions are described by irreps Γ_3^+ , M_2^+ and R_3^+ , and their interaction with octahedral rotations are well-established.⁵

Unusually high-valence states or e_g^1 electrons in *delocalized* band states will also produce structural distortions, but in most cases will preserve the uniformity of the B –O bonds and the octahedral crystal field of the BO_6 units in the process.⁶ The B cations will readily adopt mixed valence configurations, e.g. doped perovskites manganites⁷ (containing nominally both Mn^{3+} and Mn^{4+}) and also stoichiometric nickelates⁸ (Ni^{3+}) and ferrates⁹ (Fe^{4+}). The TM cation will not maintain an integer valence state (n) uniformly on all B -sites, but rather charge disproportionate (CDP); the simplest case being into two sites as

$$2B^{n+} \rightleftharpoons B_{\text{site 1}}^{(n-\delta)+} + B_{\text{site 2}}^{(n+\delta)+},$$

where δ is a fraction of an electron transferred between B -sites. Electronic correlation and on-site Coulomb repulsion effects will prefer to order the valence deviations δ so that the inequivalent lattice sites, 1 and 2, form a periodic arrangement, changing the translational symmetry. This so-called *charge ordering* (CO) lowers the potential energy of the crystal and gaps the Fermi surface.¹⁰

The electronic charge ordering is distinguishable¹¹ by an associated structural change in the local BO_6 building blocks (Figure 1). It appears as a B –O bond disproportionation or “breathing distortion,” which causes the octahedra to either dilate (site 1) or contract (site 2) according to the charge δ transferred between sites,¹² largely

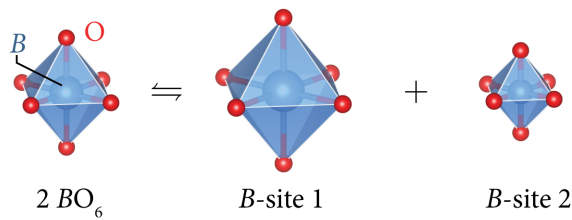


FIG. 1. (Color online.) Illustration of the effect of charge disproportionation (CDP) on the local BO_6 octahedral site equivalence. Before the CDP transition all octahedra are equivalent (left); afterwards the BO_6 octahedra disproportionate into non-equivalent sites with the simplest two-site case shown here: charge transfer between B -sites causes one octahedron to dilate (site 1) and the other octahedron to contract (site 2), resembling a “breathing” mode of the BO_6 perovskite building blocks.

because of the change in ionic radii, *i.e.*, the effective radius of $B^{(n-\delta)+}$ is larger than $B^{(n+\delta)+}$.

The magnitude of the octahedral rotations are modified by these changes in the B -O bond lengths. The extent to which cooperation between octahedral breathing and rotation instabilities is necessary to stabilizing charge order and MI-transitions, however, is not as well understood^{9,13} as the role of Jahn-Teller distortions on electronic transitions.^{5,14} To this end, group theoretical methods are particularly powerful to address the interactions among the multiple octahedron-derived instabilities. They provide a rigorous means to evaluate the symmetry allowed interactions between coupled lattice degrees of freedom, and thus, allow us to glean insight into the microscopic atomic structural contribution to the electronic CO transition in perovskite oxides.

In this work, we enumerate the space group and order parameter relationships for the octahedral breathing distortions, which are associated with irreps M_1^+ and R_1^+ of the aristotype cubic phase and the 15 simple octahedral rotation patterns available to bulk ABO_3 perovskites. We provide a list of symmetries that perovskite oxides with charge order tendencies and octahedral rotations could adopt—not all linear combinations of the instabilities are anticipated to be symmetry allowed.¹⁵ Using this information, we then illustrate how to quantify relative contributions of octahedral breathing distortions and rotations across phase boundaries in prototypical nickelate and bismuthate perovskites. This rigorous mapping of the unit-cell level structural distortions into a symmetry-adapted basis enables us to glean disentangle the role that the *atomic structure* plays in directing the macroscopic *electronic* metal–insulator transitions. Finally, we show that a synergistic combination of group-theoretical analysis with statistical analysis makes it possible to understand the complex interplay pervasive in mixed-metal perovskite oxides.

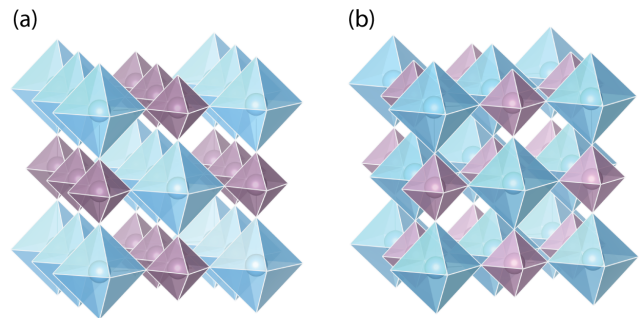


FIG. 2. (Color online.) Schematic octahedral representations of the two cooperative structural breathing distortions that coexists with charge ordering in ABO_3 perovskites. In (a) the breathing distortion is two-dimensional, irrep M_1^+ , and produces a columnar ordering of the two B cations reducing the symmetry to $P4/mmm$. In (b) a three-dimensional ordering produces a checkerboard arrangement of the B -cations and is described by the R_1^+ irrep ($Fm\bar{3}m$ symmetry).

II. COOPERATIVE BREATHING DISTORTIONS

The octahedral breathing distortions, which create two unique crystallographic B -sites, must tile in three-dimensions to maintain the corner-connectivity of the BO_6 framework—the defining feature of the perovskite crystal structure. Here we consider B -O distortions with wavevectors commensurate with the $Pm\bar{3}m$ lattice periodicity, *i.e.*, those modes which occur on the edges and corner of the simple cubic Brillouin zone. The two main *cooperative* breathing distortions (CBD) are illustrated in **Figure 2**. Note that the irreps, which we describe next, are defined using the $Pm\bar{3}m$ setting of the ABO_3 perovskites with the B cation located at the origin.

The first type of CBD consists of two BO_6 building blocks which are tiled to form a columnar arrangement of dilated and contracted octahedra [Fig. 2(a)], that splits the B -O bond lengths into a doublet and quartet.¹⁶ This distortion is associated with the active three-dimensional irrep M_1^+ with order parameter $(a, 0, 0)$ and manifests as a zone edge $k = (\frac{1}{2}, \frac{1}{2}, 0)$ lattice instability of the cubic phase. The order parameter (OP) describes a vector in the irrep space and corresponds to specific directions along which the physical distortion may be induced. For the M_1^+ irrep, the OP can have three general components (a, b, c) , where the values a , b and c correspond to amplitudes of the two-dimensional breathing distortion along each Cartesian direction x , y and z , respectively. Here we consider only the case where $b = c = 0$, *i.e.* a restricted one-dimensional space. The possible directions for the OP correspond to $(a, 0, 0)$, $(0, a, 0)$ and $(0, 0, a)$ or columnar arrangements of the CBD along the x -, y - and z -directions, respectively, so that the octahedra distort in the same sense along the given direction. As a result, the symmetry is reduced to tetragonal, $P4/mmm$ (space group no. 123), and the B -site Wyckoff position of the cubic aristotype is split as $1a \rightarrow 1a + 1c$, doubling the number of perovskite

TABLE I. Crystallographic data including the occupied Wyckoff positions (Wyck. Site) for the cooperative breathing distortions (CBD) available to ABO_3 perovskites (Figure 2) in the absence of BO_6 rotations. Atom positions are given relative to the ideal cubic symmetry such that the relevant CBD imposed on the oxygen positions is indicated by Δ . The value of Δ controls the amplitude of the B -O contraction (elongation) and typically scales with the amount of inter-site charge transfer (δ). The change in cell size is given relative to the pseudo-cubic (pc) lattice constant a_{pc} .

$M_1^+ (a, 0, 0)$		$a = b \sim \sqrt{2}a_{pc}, c \sim a_{pc}$		
$P4/mmm$ (no. 123)		$\alpha = \beta = \gamma = 90^\circ$		
Atom	Wyck. Site	x	y	z
A	2e	0	$\frac{1}{2}$	$\frac{1}{2}$
B(1)	1a	0	0	0
B(2)	1c	$\frac{1}{2}$	$\frac{1}{2}$	0
O(1)	4j	$\frac{1}{4} + \Delta$	$\frac{1}{4} + \Delta$	0
O(2)	1b	0	0	$\frac{1}{2}$
O(3)	1d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

$R_1^+ (a)$		$a = b = c \sim 2a_{pc}$		
$Fm\bar{3}m$ (no. 225)		$\alpha = \beta = \gamma = 90^\circ$		
Atom	Wyck. Site	x	y	z
A	8c	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
B(1)	4a	0	0	0
B(1)	4b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
O	24e	$\frac{1}{4} + \Delta$	0	0

formula units (f.u.) in the primitive cell (Table I).

The second CBD consists of BO_6 octahedra which are tiled in a three-dimensional checkerboard arrangement [Fig. 2(b)]. The distortion is described by a one-dimensional irrep R_4^+ and occurs as a $k = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ zone-corner lattice instability. Consequently, in the absence of other distortions, the CBD lifts the B -site equivalence while maintaining the O_h symmetry of the octahedra through uniform contraction and elongation of the B -O bonds about the trigonal axis, splitting the B -site Wyckoff position and forming a larger unit cell (Table I). We note that this type of B -site ordering is common in double perovskites with multiple B cations that show large ionic size and/or considerable oxidation state differences, *e.g.*, Ba_2MgWO_6 .¹⁷ But here, we consider only single (chemical species) B cations with different nominal valences.

III. OCTAHEDRAL ROTATION AND CBD SPACE GROUPS

A. Methodology

To enumerate the allowed combinations of CBD and octahedral rotations in perovskite oxides we use the group theoretical program ISOTROPY.¹⁸ We follow the approach

of Stokes *et al.*¹⁹ and consider the changes in lattice symmetry due to the interaction of each CBD pattern (Figure 2) with the 15 octahedral rotation systems derived from the M_3^+ and R_4^+ three-dimensional irreps describing rotations.² The advantage of this approach is that group-sub-group relationships can be established between structural variants, enabling the understanding of the structural and electronic CO transitions within a first- or second-order theory. It should be noted that the analysis of *charge* order at a particular site in the crystal is effectively the same as analyzing the effects of *cation* order due to an order-disorder transition, because both valence and chemical species split a Wyckoff position identically. In the latter case, the irrep describes a “composition” mode and reflects the site occupancy.

In this work, we enumerate those mode combinations with well-defined cooperative breathing distortions that are most likely to be observed experimentally. Although the rock salt B cation order has been studied previously in ABO_3 perovskites, the layered ordering of B cations, *i.e.* irrep M_1^+ , was examined only for the compositionally complex quadruple perovskite $A_4BB'_3O_{12}$ oxides.²⁰ Here, we report the results of the M_1^+ irrep on simple ABO_3 perovskites in the context of the CBD behavior, where cell-doubling occurs. Specifically for the M_1^+ irrep, we retain only those structures with an OP-direction $(a, 0, 0)$ such that the second and third components are zero, unless an octahedral rotation permits it to be non-zero by symmetry. Furthermore, we follow the convention introduced in Ref. 2 and 21 and only keep structures with coherent rotations—those with a fixed “sense” about each axis. We remove structure variants from our analysis which would allow for a modulation in the amplitude and sense of the rotations about a single axis.

B. Space Groups

We enumerate the space groups (Table II) and associated octahedral tilt pattern, irreps, lattice vectors, and origin allowed by group theory. We follow Glazer’s established notation²² to denote the magnitude and phase of octahedral tilt patterns in perovskites: The description of octahedral rotations are encoded using the syntax $a^\#b^\#c^\#$, where letters a , b , and c indicate rotations of BO_6 units of equal or unequal magnitude about Cartesian x -, y -, and z -axes. Note that in the case of equal magnitude rotations about different axes, the equivalent letter is duplicated, *e.g.*, $a^\#a^\#a^\#$. The superscript $\#$ can take three values: 0, +, or −, for no rotations, in-phase rotations (neighboring octahedra along a Cartesian axis rotate in the same direction), or out-of-phase rotations (adjacent octahedra rotate in the opposite direction), respectively.

Table II provides the possible space group symmetries compatible with CBD and octahedral rotations. The structural data is divided into three main blocks: The first section contains the space group symmetries in the absence of CBD; the second section enumerates the sym-

TABLE II. Possible crystallographic space groups, octahedral rotation patterns and unit cell relationships for ABO_3 perovskites exhibiting rotations of octahedra given by irreps M_3^+ and R_4^+ with order parameter directions given in parentheses (η_i, η_j, η_k) with the CBD M_1^+ or R_1^+ . The lattice vectors and origin shifts are given with respect to the high symmetry 5-atom $Pm\bar{3}m$ structure (B cation at the origin).

space group	tilt pattern	Order parameter direction		lattice vectors	origin
		M_3^+	R_4^+		
221 $Pm\bar{3}m$	$a^0 a^0 a^0$	(0,0,0)	(0,0,0)	(1, 0, 0), (0, 1, 0), (0, 0, 1)	(0, 0, 0)
127 $P4/mbm$	$a^0 a^0 c^+$	(a,0,0)	(0,0,0)	(1, 1, 0), ($\bar{1}$, 1, 0), (0, 0, 1)	(0, 0, 0)
139 $I4/mmm$	$a^0 b^+ b^+$	(a,0,a)	(0,0,0)	(0, 2, 0), (0, 0, 2), (2, 0, 0)	($\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$)
204 $Im\bar{3}$	$a^+ a^+ a^+$	(a,a,a)	(0,0,0)	(2, 0, 0), (0, 2, 0), (0, 0, 2)	($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)
71 $Immm$	$a^+ b^+ c^+$	(a,b,c)	(0,0,0)	(2, 0, 0), (0, 2, 0), (0, 0, 2)	($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)
140 $I4/mcm$	$a^0 a^0 c^-$	(0,0,0)	(a,0,0)	(1, 1, 0), ($\bar{1}$, 1, 0), (0, 0, 2)	(0, 0, 0)
74 $Imma$	$a^0 b^- b^-$	(0,0,0)	(a,0,a)	(0, 1, 1), (2, 0, 0), (0, 1, $\bar{1}$)	(0, 0, 0)
167 $R\bar{3}c$	$a^- a^- a^-$	(0,0,0)	(a,a,a)	($\bar{1}$, 1, 0), (0, $\bar{1}$, 1), (2, 2, 2)	(0, 0, 0)
12 $C2/m$	$a^0 b^- c^-$	(0,0,0)	(a,0,b)	(0, $\bar{2}$, 0), (2, 0, 0), (0, 1, $\bar{1}$)	($\frac{1}{2}, \frac{1}{2}, 0$)
15 $C2/c$	$a^- b^- b^-$	(0,0,0)	(a,b,a)	(2, $\bar{1}$, $\bar{1}$), (0, 1, $\bar{1}$), (0, 1, 1)	($\frac{1}{2}, \frac{1}{2}, 0$)
2 $P\bar{1}$	$a^- b^- c^-$	(0,0,0)	(a,b,c)	(0, 1, 1), (1, 0, 1), (1, 1, 0)	(0, 0, 0)
63 $Cmcm$	$a^0 b^+ c^-$	(0,0,a)	(b,0,0)	(2, 0, 0), (0, 0, $\bar{2}$), (0, 2, 0)	($\frac{1}{2}, 0, \frac{1}{2}$)
62 $Pnma$	$a^+ b^- b^-$	(0,a,0)	(b,0,b)	(0, 1, 1), (2, 0, 0), (0, 1, $\bar{1}$)	(0, 0, 0)
11 $P2_1/m$	$a^+ b^- c^-$	(0,a,0)	(b,0,c)	(0, $\bar{1}$, 1), (2, 0, 0), (0, 1, 1)	(0, 0, 0)
137 $P4_2/nmc$	$a^+ a^+ c^-$	(0,a,a)	(b,0,0)	(2, 0, 0), (0, 2, 0), (0, 0, 2)	(0, 0, $\bar{1}$)
<hr/>					
		M_1^+			
127 $P4/mbm$	$a^0 a^0 c^0$ ^a	(a,0,0) ^b	(0,0,0)	(1, 1, 0), ($\bar{1}$, 1, 0), (0, 0, 1)	(0, 0, 0)
83 $P4/m$	$a^0 a^0 c^+$	(a,0,0)	(b,0,0)	(1, 1, 0), ($\bar{1}$, 1, 0), (0, 0, 1)	(0, 0, 0)
74 $Imma$	$a^+ a^0 c^0$	(a,0,0)	(0,0,b)	(0, 2, 0), (0, 0, 2), (2, 0, 0)	(0, 0, 0)
69 $Fmmm$	$a^+ a^+ c^0$	(a,0,0)	(0,b,b)	(0, $\bar{2}$, 0), (2, 0, 2), ($\bar{1}$, 1, 1)	($\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$)
12 $C2/m$	$a^+ b^+ c^+$	(a,0,0)	(b,c,d)	($\bar{2}$, 2, 0), (0, 0, $\bar{2}$), (0, 2, 0)	($\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}$)
124 $P4/mcc$	$a^0 a^0 c^-$	(a,0,0)	(0,0,0)	(1, 1, 0), ($\bar{1}$, 1, 0), (0, 0, 1)	(0, 0, 0)
63 $Cmcm$	$a^- a^0 c^0$	(a,0,0)	(0,0,b)	(0, 2, 0), (0, 0, 2), (2, 0, 0)	(0, 0, 0)
51 $Pmma$	$a^- a^- c^0$	(a,0,0)	(0,0,0)	(0, 0, 2), (1, 1, 0), ($\bar{1}$, 1, 0)	(0, 0, 0)
13 $P2/c$	$a^- a^- c^-$	(a,0,0)	(0,0,0)	(1, 1, 0), ($\bar{1}$, 1, 0), (0, 0, 2)	(0, 0, 0)
15 $C2/c$	$a^0 b^- c^-$	(a,0,0)	(0,0,0)	(2, 0, 0), (0, 2, 0), (0, 0, 2)	(0, 0, 0)
11 $P2_1/m$	$a^- b^- c^0$	(a,0,0)	(b',0,0) ^c	($\bar{1}$, 1, 0), (0, 2, 0), (1, 1, 0)	(0, 0, 0)
2 $P\bar{1}$	$a^- b^- c^-$	(a,0,0)	(b',0,0) ^c	(1, 1, 0), ($\bar{1}$, 1, 0), (0, 0, 2)	(0, 0, 0)
52 $Pnna$	$a^0 b^+ c^-$	(a,0,0)	(0,0,b)	(0, 0, 2), (0, 2, 0), ($\bar{2}$, 0, 0)	(0, 0, 0)
62 $Pnma$	$a^+ b^- c^0$	(a,0,0)	(0,0,b)	(0, 2, 0), (0, 0, 2), (2, 0, 0)	(0, 0, 0)
11 $P2_1/m$	$a^- b^- c^+$	(a,0,0)	(b,0,0)	($\bar{1}$, 1, 0), (0, 2, 0), (1, 1, 0)	(0, 0, 0)
68 $Ccca$	$a^+ a^+ c^-$	(a,0,0)	(0,b,b)	(2, 2, 0), ($\bar{2}$, 2, 0), (0, 0, 2)	(2, 0, 0)
<hr/>					
		R_1^+			
225 $Fm\bar{3}m$	$a^0 a^0 a^0$ ^d	(a)	(0,0,0)	(2, 0, 0), (0, 2, 0), (0, 0, 2)	(0, 0, 0)
128 $P4/mnc$	$a^0 a^0 c^+$	(a)	(b,0,0)	(1, 1, 0), ($\bar{1}$, 1, 0), (0, 0, 2)	(0, 0, 0)
201 $Pn\bar{3}$	$a^+ a^+ a^+$	(a)	(b,b,b)	(0, 0, $\bar{2}$), (0, $\bar{2}$, 0), ($\bar{2}$, 0, 0)	(1, 1, 1)
134 $P4_2/nmm$	$a^0 b^+ b^+$	(a)	(b,b,0)	(0, 0, 2), (2, 0, 0), (0, 2, 0)	(0, $\bar{1}$, 0)
48 $Pnnn$	$a^+ b^+ c^+$	(a)	(b,c,d)	(2, 0, 0), (0, 0, 2), (0, 2, 0)	(0, 0, 0)
148 $R\bar{3}$	$a^- a^- a^-$	(a)	(0,0,0)	($\bar{1}$, 1, 0), (0, $\bar{1}$, 1), (2, 2, 2)	(0, 0, 0)
87 $I4/m$	$a^0 a^0 c^-$	(a)	(0,0,0)	($\bar{1}$, 1, 0), ($\bar{1}$, $\bar{1}$, 1), (0, 0, 2)	(0, 0, 0)
12 $C2/m$	$a^0 b^- b^-$	(a)	(0,0,0)	($\bar{1}$, 2, 1), (1, 0, 1), (0, 2, 0)	(0, 0, 0)
2 $P\bar{1}$	$a^- b^- c^-$	(a)	(0,0,0)	(1, 0, 1), (1, 1, 0), ($\bar{1}$, 1, 0)	(0, 0, 0)
15 $C2/c$	$a^0 b^+ c^-$	(a)	(b,0,0)	(2, 0, 0), (0, 2, 0), (0, 0, 2)	($\frac{1}{2}, \frac{1}{2}, 0$)
86 $P4_2/n$	$a^+ a^+ c^-$	(a)	(b,b,0)	(0, 0, 2), (2, 0, 0), (0, 2, 0)	($\bar{1}$, $\bar{1}$, 0)
14 $P2_1/c$	$a^+ b^- b^-$	(a)	(b,0,0)	(1, $\bar{1}$, 0), (1, 1, 0), (1, $\bar{1}$, 2)	(0, 0, 0)

^a In the absence of octahedral rotations, the axes are unique due to the CBD.

^b The CBD makes the z-direction unique.

^c The b' denotes that this is a secondary distortion that is symmetry allowed. In this case in-phase rotations about the z-direction. The Glazer tilt is defined for the case $b' = 0$.

^d The R_1^+ mode acts along the body diagonal and does not create a unique axis in the crystal as in the case of the three-dimensional M_1^+ irrep. Only the octahedral rotations lifts the axes equivalence.

metries that result from the planar CBD with octahedral rotations; and the third section includes those obtained from the three-dimensional CBD combined with rotations. Structures appearing in bold in Table II correspond to

CBD without any octahedral rotations and are given first at the top of block two and three. Note that for perovskites with rotations and the M_1^+ CBD, there is more than one structure possible because of the relative orien-

TABLE III. The change in space group which occurs when the different octahedral CBD are combined with the 15 simple octahedral tilt systems.

Tilt system (Glazer notation)	No Breathing	M_1^+	R_1^+
$a^0a^0a^0$	$Pm\bar{3}m$	$P4/mmm$	$Fm\bar{3}m$
$a^0a^0c^+$	$P4/mbm$	$P4/m$	$P4/mnc$
		$Imma$	
$a^0b^+b^+$	$I4/mmm$	$Fmmm$	$P4_2/nmm$
$a^+a^+a^+$	$Im\bar{3}$	none	$Pn\bar{3}$
$a^+b^+c^+$	$Immm$	$C2/m$	$Pnnn$
$a^0a^0c^-$	$I4/mcm$	$P4/mcc$	$I4/m$
		$Cmcm$	
$a^0b^-b^-$	$Imma$	$Pmma$	$C2/m$
$a^-a^-a^-$	$R\bar{3}c$	none	$R\bar{3}$
$a^0b^-c^-$	$C2/m$	$C2/c$	none
		$P2_1/m$	
$a^-b^-b^-$	$C2/c$	$P2/c$	none
$a^-b^-c^-$	$P\bar{1}$	no change	no change
$a^0b^+c^-$	$Cmcm$	$Pnna$	$C2/c$
		$Pnma$	
$a^+b^-b^-$	$Pnma$	none	$P2_1/c$
$a^+b^-c^-$	$P2_1/m$	$P2_1/m$	none
$a^+a^+c^-$	$P4_2/nmc$	$Ccca$	$P4_2/n$

tation of the tilt pattern with respect to the columnar arrangement of dilated and contracted octahedra.

Table II directly reveals the effect of the octahedral rotations and the CBD on the crystal symmetry lowering. Consider the middle block (order parameter directions M_1^+ , M_3^+ , and R_4^+). The seemingly similar tilt patterns $a^0a^0c^+$ and $a^+a^0c^0$ – depending on the crystallographic axes they act upon – yield two completely different space groups, $P2/m$ and $Imma$ respectively. Furthermore, there are a number of space groups appearing in each of the blocks of Table II: $C2/m$ appears both in the rotation only block (sans any CBD) and in the third block with the R_1^+ CBD. Formally the crystallographic symmetries are identical in each case; however, physically the rotation patterns adopted by the crystals are different. When only R_4^+ rotations with order parameter $(a, 0, b)$ are present in the crystal structure, space group $C2/m$ allows the out-of-phase rotations about the y - and z -axes to be of different magnitude. In the presence of the three-dimensional CBD (R_1^+) only the $a^0b^-b^-$ and not the $a^0b^-c^-$ rotation is compatible with the $C2/m$ symmetry, whereas in the case of identical rotations without CBD a higher symmetry $Imma$ phase results. Such restrictions imposed on the rotation axes equivalence are described next, and for the reason previously described explains why “none” appears as an entry in Table III.

C. Compatible CBD and Rotation Symmetries

In Table III, we collectively analyze how the M_1^+ and R_1^+ irreps change the space group symmetry when com-

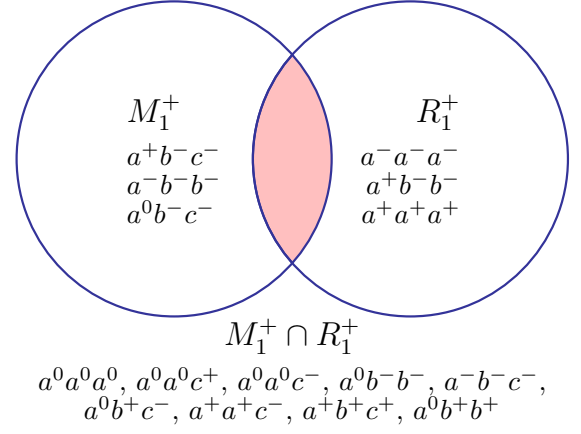


FIG. 3. (Color online.) Representation of the rotation patterns that are compatible with each (or both, given by the intersection of the) CBD without requiring a further symmetry reduction.

bined with each of the 15 simple octahedral tilt systems. This information is schematically shown in Figure 3. Only one symmetry exists, $P\bar{1}$, where the breathing distortion is geometrically compatible with the symmetry of the perovskite structure with octahedral rotations alone ($a^-b^-c^-$), meaning “no change” in unit cell or translational symmetry is required to accommodate the multiple distortions. Table III also reveals that the $P2_1/m$ symmetry is compatible with two different octahedral rotation patterns and the 2D M_1^+ CBD: $a^0b^-c^-$ and $a^+b^-c^-$. While $P\bar{1}$ is compatible with both M_1^+ and R_1^+ irreps, $P2_1/m$ only exists for the M_1^+ irrep.

For entries containing “none,” the symmetry of the combined rotation pattern and CBD are incompatible, indicating that a further symmetry reduction would be required if the energetically stable phase prefers an atomic structure with both flavors of those distortions. This is made clear by examining the $a^-a^-a^-$ rotation pattern, which corresponds to an equal amplitude of out-of-phase rotations about each axis, or equivalently a single out-of-phase rotation about the three-fold axis. The trigonal symmetry is incompatible with a two-dimensional distortion that would require a loss of the three-fold axis and therefore need at a minimum a symmetry reduction to a lattice with tetragonal geometry. Thus, ‘none’ appears in the M_1^+ column corresponding to the row with the $a^-a^-a^-$ rotation pattern. Such incompatibility with the M_1^+ CBD is alleviated if the rotation pattern already exhibits anisotropy, e.g., $a^-b^-b^-$, yielding space group $P2/c$ (Table III).

IV. STRUCTURAL TRANSITIONS

Although the microscopic origin for charge disproportionation results from an electronic instability related to the electronic configuration of a particular metal center, the cooperative ordering of the CDP leads to a macro-

scopic bond-disproportionation. In the displacive limit, the two unique and nearly uniform octahedra result, dilating and contracting in proportion to the magnitude of charge transfer. Across the electronic phase transitions, the breathing distortions can couple directly to octahedral rotations. (We do not consider here indirect coupling through a common strain component.)

Here we describe the effect of coupling between the common orthorhombic rotation pattern ($a^+b^-b^-$) obtained from irreps $M_3^+ \oplus R_4^+$, which gives the six-dimensional order parameter with two unique directions as

$$(\eta_+, 0, 0, 0, \eta_-, \eta_-).$$

The addition of the three-dimensional CBD R_1^+ to the rotation pattern gives a seven-dimensional order parameter space, *i.e.*, $(\beta, \eta_+, 0, 0, 0, \eta_-, \eta_-)$, which we contract to an effective four-dimensional space to obtain the $P2_1/c$ space group (cf. Table II). Without assuming which transition occurs first—whether the rotations precede or follow the CBD—we construct a Landau free energy expansion about the cubic phase ($\beta = \eta_+ = \eta_- = 0$) as

$$\mathcal{F}(\beta, \eta_i) = \phi^2 + \phi^4 + C_1\beta^2\eta_+^2 + C_2\beta^2\eta_-^2 + D_3\eta_+^2\eta_-^2,$$

where ϕ^2 and ϕ^4 describe the homogeneous quadratic and quartic terms for each order parameter, and C_i are the coefficients coupling the CBD to the in- or out-of-phase rotations, and D_3 describes the biquadratic coupling of the different BO_6 rotation “senses” in the $a^+b^-b^-$ tilt pattern.

The group-subgroup relationships that occur as result of the coupling are depicted in Figure 4. Intriguingly, the rotations and the CBD couple biquadratically, which indicates that the interactions across the transitions could be either cooperative or antagonistic. It is possible that the particular rotations could suppress CO by eliminating the structural octahedral breathing distortion altogether through the interaction term. However, in most cases, the rotation amplitudes are weakly modified across the electronic CO transition, suggesting that the strength of the coupling C_i is in general small. We investigate this in the Section V through a statistical approach. We also note that while the order of the coupling is important, the difference in temperature scales at which the rotation and charge ordering occurs is also important in determining how the structural order parameters influence each other. The strongest interaction occurs when the temperatures are similar, while if they are far apart, the two structural transitions will weakly couple.

V. STRUCTURE-FUNCTIONALITY RELATIONSHIPS

In this section, we apply our group theory results to quantitatively explore the relationship between structure and physical properties of experimentally known rare-earth nickelate and bismuthate perovskites. There is a

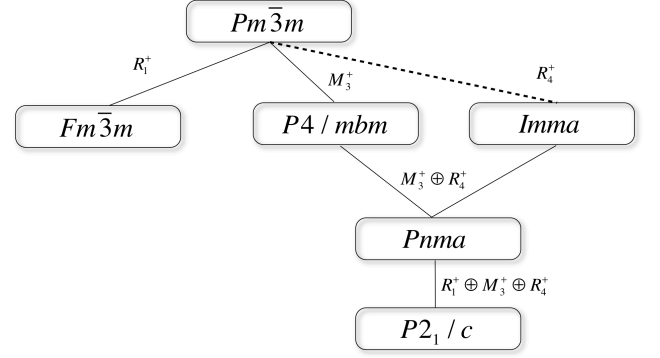


FIG. 4. Group-sub-group relationship between $Pm\bar{3}m$ and $P2_1/c$. Irreps within $Pm\bar{3}m$ responsible for transitions are shown. Dotted line indicates that the phase transition is not continuous within the confines of Landau theory.

significant interest in developing strategies – both experimentally and theoretically – to rationally control octahedral distortions through the interplay of chemical pressure, epitaxial strain engineering, and ultrathin superlattice heterostructure formation.^{1,23–28} Although several octahedral distortion metrics, *e.g.*, the crystallographic tolerance factor or bending of the $B-O-B$ bond angle,^{29,30} have played an important role in the understanding of the electronic and magnetic properties of perovskite oxides,³¹ they have had limited success in materials design. Knowledge of quantitative structure-property octahedral distortion relationships are required to accelerate materials discoveries.

Distortion-mode decomposition analysis is an alternative approach^{5,18,32} (widely practiced and followed in the crystallography literature) to study displacive³³ phase transitions in perovskites. It involves describing a distorted (low-symmetry) structure as arising from a (high-symmetry) parent structure with one or more static symmetry-breaking structural distortions.³² In the undistorted parent structure, each symmetry breaking distortion-mode has zero amplitude. The low-symmetry phase, however, will have finite amplitudes for each irrep compatible with the symmetry breaking. Said another way, the low-symmetry phase is rigorously described through a series expansion of the symmetry breaking structural modes that “freeze” into the parent structure. Critically, the weights or amplitudes assigned to each irrep are obtained according to the contribution that each irrep is present *and* the requirement that linearity is maintained.

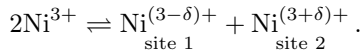
What is of particular utility in formulating quantitative relationships connecting octahedral distortions, which are now described mathematically, to macroscopic properties for materials design is that each irrep carries a physical representation of the displacive distortions—the unique atomic coordinates describing various symmetry-adapted structural modes. The relative importance of these modes on properties may then be mapped by means of *ab initio* computational methods.³⁴ Accessibility to

computational methods make the distortion-mode analysis powerful, because it is possible to independently study various distortions (irreps) and directly assess their role in structural and electronic phase transition mechanisms. Furthermore, the distortion-mode analysis relies solely on crystal structural data, which enables both bulk and thin film materials alike to be evaluated on equal-footing. Such direct comparison is not possible through aggregate parameters such as the tolerance factor, *i.e.* when the composition is fixed, or other metrics widely followed in the literature.

In the remainder of this section, we use the distortion-modes to form the basis for the quantitative description of octahedral distortions and CBD on material properties. Using bulk $R\text{NiO}_3$, where R is a rare-earth element, and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ perovskite compounds as prototypical charge-ordering materials, we decompose available low-symmetry structural data into symmetry-adapted structural distortion modes. We then evaluate and correlate the amplitudes of the distortion-modes to macroscopic materials behavior to uncover trends linking octahedral distortions to the structural and physical properties. We use the group-theory program ISODISTORT¹⁸ for distortion-mode decomposition analysis and R^{35,36} for the statistical analysis. For readers interested in reproducing our work, we have deposited the raw data and the R-script in the supplementary materials section available at <http://link.aps.org/supplemental/XYZ>.

A. $R\text{NiO}_3$ Nickelates

Rare-earth perovskite nickelates, $R\text{NiO}_3$, where $R = \text{Y}, \text{Ho}, \text{Er}, \text{Dy}, \text{Lu}, \text{Pr}, \text{or Nd}$, exhibit non-trivial changes in structure and physical properties, including sharp first-order temperature-driven MI-transitions, unusual antiferromagnetic order in the ground state, and site- or bond-centered charge disproportionation.^{29,37,38} At the MIT temperature (T_{MI}), the crystal symmetry lowers from orthorhombic $Pbnm$ to monoclinic $P2_1/c$ symmetry³⁹ (Figure 4), where the Ni cation no longer maintains a unique uniform valence on all sites, and disproportionates as



Moreover, the insulating ground-state displays a complex antiferromagnetic order (Type- E') below a Néel temperature (T_N). Several studies^{29,30,40–42} in the past have suggested the likely existence of a complex interplay between octahedral rotations, transport, and magnetic properties. To extract deeper insight into these interrelationships, we (i) identify all active distortion modes in each composition, (ii) determine the individual amplitudes for each modes, and (iii) explore the statistical correlation between individual distortion-modes and the physical properties, specifically T_{MI} and T_N .

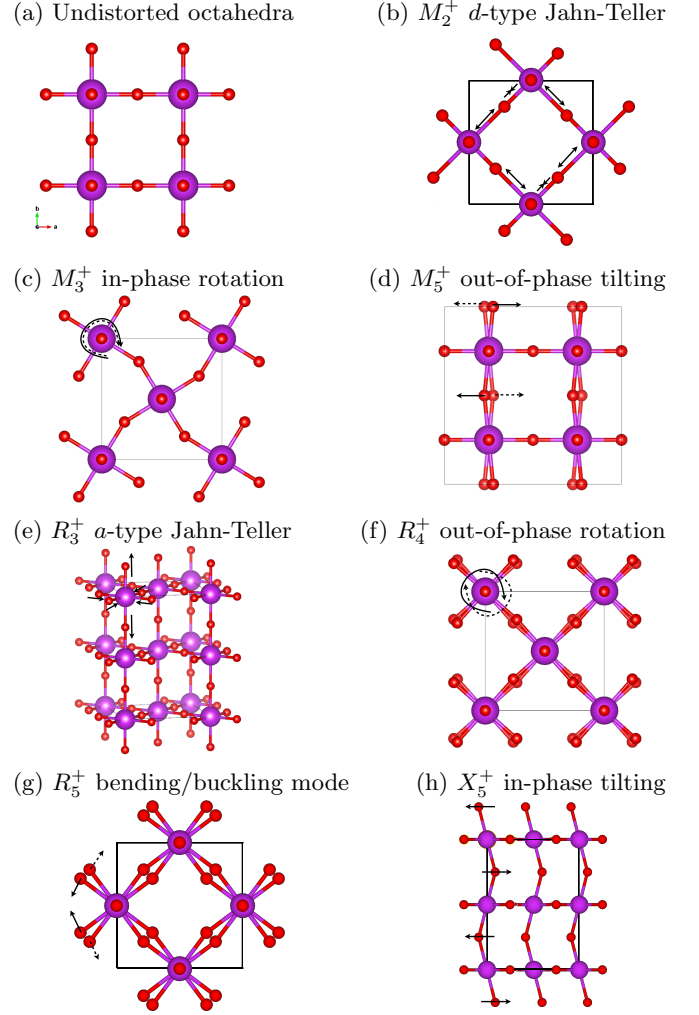


FIG. 5. (Color online.) Illustration of the symmetry-adapted orthonormal distortion modes found in the low-symmetry $R\text{NiO}_3$ and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ perovskites. The undistorted octahedra are shown in panel (a) for comparison. Octahedral tilting distortions refer to the rotation of the octahedral units (we use ‘tilting’ and ‘rotation’ interchangeably). The out-of-phase distortions are differentiated using arrows (lines and dashes) indicating the direction of cooperative atomic displacements. (b) M_2^+ is the d -type Jahn-Teller mode, where two bonds shrink and two elongate; (c) M_3^+ is an in-phase rotation mode; (d) M_5^+ is an out-of-phase tilting mode; (e) R_3^+ is the a -type Jahn-Teller mode, where four bonds contract and two expand, and *vice versa*; (f) R_4^+ is an out-of-phase rotation mode; (g) R_5^+ is an out-of-phase bending mode; (h) X_5^+ is an in-phase tilting mode accompanied by A cation displacements, which are not shown for clarity.

1. Structure Decomposition

We follow the procedure outlined by Campbell *et al.*¹⁸ to decompose the $P2_1/c$ monoclinic crystal structure data, obtained from previously published diffraction studies,^{43–46} into the orthonormal symmetry-modes.

Diffraction data for YNiO_3 , ErNiO_3 , LuNiO_3 , and HoNiO_3 were measured at 295 K; DyNiO_3 at 200 K; NdNiO_3 at 50 K; and finally, PrNiO_3 at 10 K. T_{MI} and T_N were obtained from the review article by Catalan.³⁰

The $P2_1/c$ structure decomposes into eight algebraically independent distortion-modes corresponding to the following irreps: R_1^+ , R_3^+ , R_4^+ , R_5^+ , X_5^+ , M_2^+ , M_3^+ , and M_5^+ . The physical representation of each irrep and the consequence on the octahedral framework are schematically illustrated in Figure 5. Based on the relative amplitudes of distortion-modes we obtain from ISODISTORT, the dominant modes are ranked in the following order (from most dominant to least dominant):

$$R_4^+ > M_3^+ > X_5^+ > R_5^+ > R_1^+ > M_5^+ > M_2^+ > R_3^+$$

Not surprising, the two most common octahedral distortion-modes that describe the $a^+b^-b^-$ rotation pattern, R_4^+ and M_3^+ , emerge as the dominant modes, along with that of X_5^+ , which also contains A cation displacements with relatively high amplitude. Such anti-parallel displacements of the A cations are established to be correlated with the amplitudes of the octahedral rotations in perovskites.⁴⁷ There are five other irreps, namely R_5^+ , R_1^+ , M_5^+ , M_2^+ , and R_3^+ with relatively low amplitudes. Note that the presence of the R_1^+ breathing mode in all $R\text{NiO}_3$ nickelates is the active mode involved in the symmetry lowering orthorhombic-to-monoclinic structural phase transition and is indicative of the CDP behavior.

Our distortion-mode analysis points out the relatively weak presence of two types of Jahn-Teller distortions to the NiO_6 units, M_2^+ and R_3^+ (Figure 5). This has important implications, because experimental observations based on giant oxygen $\text{O}^{16}\text{-O}^{18}$ isotope effect⁴⁰ indicate the presence of dynamic Jahn-Teller polarons; however the interpretation of orbital-ordering has lacked conclusive support from diffraction experiments.³⁰ More recently, ultra-thin films of nickelates are being increasingly investigated for rational control of orbital polarization.^{48,49} Our observation of orbital-ordering in bulk nickelates offers insights into the potential of tuning orbital polarization in epitaxial nickelate thin films. We can use the misfit strain—applied via symmetry mismatch at the thin film—substrate interface—to selectively enhance the contributions of Jahn-Teller modes, M_2^+ and R_3^+ , in nickelates that already show tendencies for orbital-ordering.⁵⁰ Alternatively, orbital-ordering could *emerge* in nickelates, *e.g.*, LaNiO_3 where the Jahn-Teller modes are prohibited by symmetry in the bulk ground-state structure, through quantum confinement effects as observed in the limits of ultra-thin films,^{48,49} although in this case, strain-induced Jahn-Teller distortions would likely result in larger energetic penalties.

2. Statistical Analysis

We now evaluate the statistical correlation between the amplitude of the symmetry-adapted modes and the

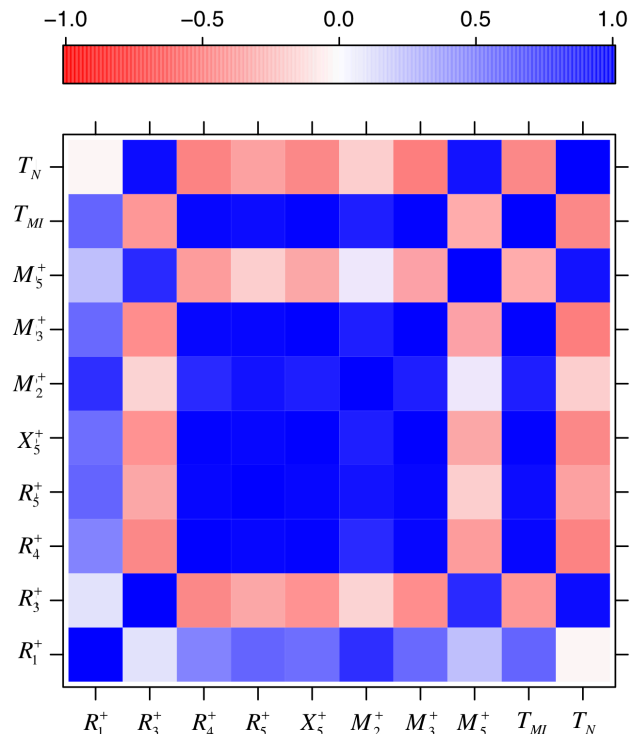


FIG. 6. (Color online.) Correlation heat map capturing the degree of linear relationship between unit cell level structural distortion modes and macroscopic transition temperatures, T_{MI} , and T_N in $R\text{NiO}_3$ perovskites. Dark blue (red) indicates a strong positive (negative) correlation and white indicates no statistical correlation between the two variables. Units for the irreps and temperatures are given in \AA and Kelvin (K), respectively.

macroscopic T_{MI} , and T_N transition temperatures. We construct a dataset containing seven $R\text{NiO}_3$ nickelates, where each rare-earth nickelate in our set is described using eight distortion-modes, T_{MI} , and T_N , resulting in a 7×10 matrix. We scaled the data by subtracting the mean of each column from its corresponding columns (this process is also known as centering), and then divided the centered columns by their standard deviations. To evaluate the degree of linear relationship between the structural distortions, T_{MI} , and T_N , we calculate the sample covariance of the centered and scaled dataset as

$$\text{Cov}[X] = \frac{1}{n-1} \sum_{i=1}^n (\bar{x}_i)(\bar{x}_j),$$

where $n = 7$ is the total number of $R\text{NiO}_3$ compounds in our dataset; \bar{x}_i and \bar{x}_j are the centered and scaled column vectors of our data matrix X , respectively. Results from the covariance analysis are summarized as a correlation heat map in Figure 6.

A strong positive correlation is found between modes capturing distortions to the NiO_6 octahedra: M_2^+ (a planar Jahn-Teller mode), M_3^+ , X_5^+ , R_4^+ , and R_5^+ modes. Even though the distortion-modes are orthonormal by

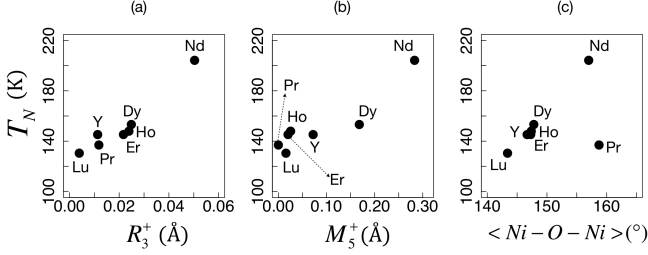


FIG. 7. (Color online.) A strong linear relationship is seen between (a) R_3^+ and the Néel temperature (T_N) with a correlation coefficient of 0.957 and (b) M_5^+ and T_N with a correlation coefficient of 0.916. In (c) we plot the average $\langle \text{Ni-O-Ni} \rangle$ bond angle and T_N to illustrate that the R_3^+ and M_5^+ irreps capture the main variation in T_N for both $T_{MI} = T_N$ and $T_{MI} > T_N$ nickelates compared to the $\langle \text{Ni-O-Ni} \rangle$ bond angle. (Experimental data from Ref. 30.)

construction, but when they are collectively evaluated for a series of RNiO_3 compounds our statistical analysis reveals that they are statistically *dependent* and coupled. These modes largely describe bond angle distortions and are positively correlated with the electronic transition T_{MI} . The conventional route to describe variations in T_{MI} primarily focus on tolerance factor and *average* Ni-O-Ni bond angle, whereby bending of Ni-O-Ni angle further from the ideal case of 180° decreases the bandwidth, promoting the insulating state over the metallic state.^{23,30,51} We indeed recover this behavior, however, we also identify the unique displacement patterns that geometrically sum to give the aggregate bond angle: irreps M_2^+ , M_3^+ , X_5^+ , R_4^+ , and R_5^+ cooperatively act to bend the Ni-O-Ni angle. These five irreps fully describe the $Pbnm$ crystal structure relative to the cubic phase found in the metallic nickelates at high-temperature, reinforcing the concept that the orthorhombic distortions are largely responsible for the bandwidth-controlled transport behavior in nickelates, and hence *prepare* the electronic system for the MIT.

Intriguingly, the R_1^+ CBD mode which is the usual signature for CO has a relatively moderate effect on T_{MI} , indicating that the dominate structural route to engineer the electronic transition may not be through isotropic bond length distortions. In fact, the a -type R_3^+ Jahn-Teller mode and the M_5^+ tilting mode do not contribute significantly to T_{MI} , and we find they are *anti-correlated* with the electronic transition temperature. Our conclusion to this point on the MI-transition is that the geometry of the oxygen framework structure in these charge-ordering oxides is the important atomic scale feature to tailor.

We now shift our attention to the Type-E' antiferromagnetic ordering. Unlike the transport behavior, where the Ni-O-Ni bond angle concept appears to be sufficient to explain its variability, the origin of antiferromagnetic ordering is much more complex. Previous high-resolution photoemission measurement⁵² and pressure dependent studies²⁹ of T_N have established the existence of two distinct regimes for RNiO_3 with $T_{MI} = T_N$ and $T_{MI} > T_N$,

indicative that simple tolerance factor and Ni-O-Ni superexchange interaction arguments cannot capture the complete physics of the system. Lee *et al.* used two-band model and Hartree-Fock theory to classify nickelates with $T_{MI} = T_N$ as itinerant, whereas those with $T_{MI} > T_N$ show stronger electron correlation.⁵³ Nonetheless, there is no unique descriptor known in the literature that captures all the variance in the T_N ordering temperature.

Our analysis reveals the existence of a strong linear relationship between T_N and two irreps, R_3^+ and M_5^+ : the three dimensional Jahn-Teller mode, where in each NiO_6 octahedron four bonds contract and two elongate, and the out-of-phase tilting mode, respectively. The linear relationship is valid for both $T_{MI} = T_N$ and $T_{MI} > T_N$ nickelates (Figure 7), indicating that R_3^+ and M_5^+ contain additional information that is not captured by either the $\langle \text{Ni-O-Ni} \rangle$ angle or tolerance factor. The R_3^+ mode is more strongly correlated with T_N than the M_5^+ mode, indicating an underlying relationship between the long-range antiferromagnetic order and the local and subtle Jahn-Teller bond distortions. We also note that R_3^+ and M_5^+ irreps appear in the monoclinic $P2_1/c$ crystal structure and are not allowed by symmetry in the $Pbnm$ orthorhombic space group.

We conjecture that with deterministic control over the atomic structure, *e.g.*, enhancing R_3^+ relative to R_4^+ or *vice versa*, it could be possible to fully decouple T_{MI} from T_N , shifting the equilibrium phase boundaries dividing the metallic/insulating states from the paramagnetic/ordered regions to create non-equilibrium phase. Although it is compelling to extend our interpretation beyond correlation to full causation, we emphasize that first-principles calculations and detailed structural characterization are essential to establish the physical origin underlying the statistical associations we have identified.

B. $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ Bismuthates

BaBiO_3 is a CO insulator which undergoes a series of phase transitions with temperature. At room temperature it has a monoclinic crystal structure with space group $I2/m$. In the monoclinic $I2/m$ structure, the octahedrally coordinated tetravalent Bi cation charge disproportionates into $\text{Bi}^{(4+\delta)+}$ and $\text{Bi}^{(4-\delta)+}$. Previous optical conductivity measurements⁵⁴ attribute the appearance of an electronic gap in the stoichiometric $I2/m$ phase to structural CBD and octahedra rotations.

Chemical doping of BaBiO_3 with potassium by random substitution on the Ba sites, $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, produces a sequence of structural and electronic phase transitions. *Increasing* the potassium concentration leads to crystal structures of *higher* symmetry: An orthorhombic $Ibmm$ phase is stable over the range $0.12 \leq x < 0.37$. At $x \approx 0.37$, a tetragonal $I4/mcm$ phase is stable and for $0.37 < x < 0.53$ BaBiO_3 transforms to $Pm\bar{3}m$ cubic.^{55,56} The electronic transport properties also evolve concomitant with these structural changes: The system transforms

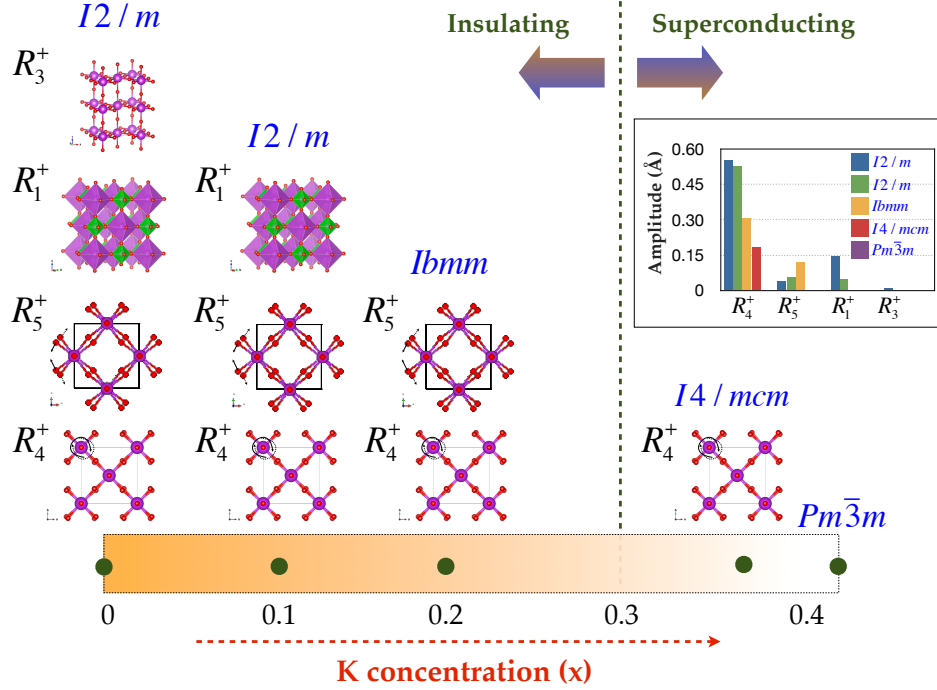


FIG. 8. (Color online.) Relationship between crystal symmetry and structural distortions in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ as a function of A site doping. The number of symmetry unique structural modes decreases with increasing K concentration. Pure BaBiO_3 is described by four modes, R_1^+ , R_3^+ , R_4^+ , and R_5^+ . As the concentration of K increases, the Jahn-Teller R_3^+ mode disappears rapidly, followed by loss of the three-dimensional CBD R_1^+ . The bar graph (inset) shows quantitatively in units of angstroms the change in amplitude of the structural modes observed in each space group.

from a robust insulating state in the monoclinic phase to semiconducting in the orthorhombic phase, and finally to a superconducting state in the tetragonal and undistorted cubic phases.

Our focus here is to systematically track the structural phase transition as a function of K doping, with emphasis placed on the role of the symmetry-adapted modes and CBD-rotation symmetries. We decompose the low-symmetry crystal structures of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ across the phase boundaries using five chemical compositions: BaBiO_3 , $\text{Ba}_{0.9}\text{K}_{0.1}\text{BiO}_3$, $\text{Ba}_{0.8}\text{K}_{0.2}\text{BiO}_3$, $\text{Ba}_{0.63}\text{K}_{0.37}\text{BiO}_3$, and $\text{Ba}_{0.60}\text{K}_{0.40}\text{BiO}_3$, for which high-resolution diffraction data exists.^{55,57}

The results from our analysis are summarized schematically in Figure 8. The $I2/m$ structure is described by four irreps R_1^+ , R_3^+ , R_4^+ , and R_5^+ , which capture the CBD, a Jahn-Teller distortion, and out-of-phase octahedral rotations, and out-of-phase bond stretching, respectively. Although the $I2/m$ monoclinic symmetry is maintained at small doping, as with $\text{Ba}_{0.9}\text{K}_{0.1}\text{BiO}_3$, our mode decomposition analysis reveals that the amplitude of the R_3^+ mode vanishes completely. The relative amplitudes of the R_1^+ breathing mode and out-of-phase octahedral rotation modes also decrease, whereas the amplitude of the out-of-phase bending distortion increases.

With further increase in K concentration, for example in $\text{Ba}_{0.8}\text{K}_{0.2}\text{BiO}_3$, the crystal structure becomes orthorhombic $Ibmm$. Interestingly, even in the absence of the CBD

distortion, which we find has zero amplitude at $x = 0.2$, the electronic structure remains insulating. At the same time, the amplitude of the R_5^+ mode continues to increase in the presence of out-of-phase octahedral rotations R_4^+ .

Upon further increase in K, the R_5^+ mode disappears completely, yielding tetragonal $I4/mcm$ $\text{Ba}_{0.63}\text{K}_{0.37}\text{BiO}_3$ with only the R_4^+ octahedral rotation mode at reduced amplitude. Across this structural transition⁵⁵, the compound becomes metallic and superconducting⁵⁵ with a critical transition temperature of 27 K. Our analysis suggests that the subtle R_5^+ distortion may play a more important role in the transport properties of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ than the commonly believed R_1^+ CBD which vanishes immediately at small potassium doping. Finally, for $x \sim 0.4$, the superconducting phase is also stable in the cubic $Pm\bar{3}m$ structure without any octahedral rotations or distortions.

Our group theoretical approach applied to the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ system, reveals systematic trends in the irreps with doping across the structural phase boundaries. One of the outstanding questions regarding the electronic properties of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is the stability of the wide semiconducting or insulating region with doping. Recently Franchini *et al.* performed density functional calculations to understand this feature of the phase diagram, attributing the insulating state to the formation of polaronic defects,⁵⁶ which are consistent with spectroscopic measurements.⁵⁸ Here, we suggest the existence of a plausible relationship between the stability of the

polaronic defects and the persistence of the R_5^+ distortion in $\text{Ba}_{0.8}\text{K}_{0.2}\text{BiO}_3$, which eventually delays the onset of superconducting phase in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ perovskite.

VI. SUMMARY

We applied group theoretical methods to evaluate the interplay between octahedral rotations and electronic charge ordering, which we parameterized structurally as octahedral “breathing” or cooperative bond length distortions through irreducible representations. We enumerated the possible space groups available to perovskites from the intersection of these distortions. This crystallographic data should prove useful for experimental structure refinements or serve as a well-defined set of symmetry-unique structures for which the stability of transition metal compounds susceptible to charge ordering may be evaluated with first-principles total energy methods.

With this information, we combined structural mode decomposition techniques with statistical methods to extract structure–property relationships from available experimental diffraction data on representative charge ordering oxides. The crystal structures of nickelates and bismuthates were decomposed in terms of symmetry adapted distortion-modes and the evolution in the amplitude of each local structure mode tracked as a function of an external chemical parameter. We illustrated that this alternative set of descriptors provides a useful construct beyond the traditional tolerance factor paradigm found in perovskites to understand the atomic scale origin of physical properties, specifically how unit cell level modifications correlate with macroscopic functionality.

Our statistical analysis uncovered previously unappreciated relationships that may be harnessed for electronic structure by design, some of which are being carried out within our group and will be reported later. We emphasize that the application of statistics to the decompositions does not require solely experimental data; the analysis may be performed with computationally obtained data alone. Importantly, the relationships established with

these techniques may be cross-validated by the construction of hybrid data sets, which combine theoretical results with experiment data, making it possible to extract and validate new insight into the material physics of oxides with correlated electrons. We anticipate that this approach will spawn a number of additional studies in diverse crystal classes since it is immediately generalizable: the synergy of applied group theoretical methods with statistical analysis and subsequent first-principles calculations provides a platform to achieve rational structure-driven design of complex materials.

ACKNOWLEDGMENTS

P.V.B. was supported by The Defense Advanced Research Projects Agency (DARPA) under grant no. N66001-12-4224. J.M.R. was supported by the U.S. Office of Naval Research (ONR), under grant number N00014-11-1-0664. The views, opinions, and/or findings reported here are solely those of the authors and do not represent official views of DARPA or ONR. We thank our group members, D. Puggioni and A. Cammarata, for useful discussions.

Appendix A

TABLE IV. Abbreviations appearing throughout the text.

CBD	Cooperative octahedral breathing distortion
TM	Transition metal (referring to a cation)
MIT	Metal-to-insulator transition
CDP	Charge disproportionate
T_{MI}	Metal-to-insulator transition temperature
T_N	Néel temperature
DFT	Density Functional Theory
T_C	Superconducting transition temperature

* jrondinelli@coe.drexel.edu

¹ J. M. Rondinelli, S. J. May, and J. W. Freeland, *MRS Bulletin* **37**, 261 (2012).

² C. J. Howard and H. T. Stokes, *Acta Crystallographica Section B* **54**, 782 (1998).

³ E. Canadell, M.-L. Doublet, and C. Iung, *Orbital Approach to the Electronic Structure of Solids* (Oxford University Press, New York, 2012).

⁴ A. J. Millis, P. B. Littlewood, and B. I. Shraiman, *Phys. Rev. Lett.* **74**, 5144 (1995).

⁵ M. A. Carpenter and C. J. Howard, *Acta Crystallographica Section B* **65**, 134 (2009); M. A. Carpenter and C. J. Howard, *Acta Crystallographica Section B* **65**, 147 (2009).

⁶ J. B. Goodenough and F. Rivadulla, *Modern Physics Letters*

B **19**, 1057 (2005).

⁷ M. B. Salamon and M. Jaime, *Rev. Mod. Phys.* **73**, 583 (2001).

⁸ J. B. Goodenough, *Reports on Progress in Physics* **67**, 1915 (2004).

⁹ J. Matsuno, T. Mizokawa, A. Fujimori, Y. Takeda, S. Kawasaki, and M. Takano, *Phys. Rev. B* **66**, 193103 (2002).

¹⁰ The MI-transition results from electronic localization, which can be intrinsic and electrostatic in nature (electron–electron repulsion), or extrinsic, due to defects or disorder.

¹¹ Y. Quan, V. Pardo, and W. E. Pickett, *Phys. Rev. Lett.* **109**, 216401 (2012); H. Park, A. J. Millis, and C. A. Marianetti, *Phys. Rev. Lett.* **109**, 156402 (2012); A. Cammarata

- and J. M. Rondinelli, *Phys. Rev. B* **86**, 195144 (2012).
- ¹² Not all charge-ordering transitions require an concomitant change in structure, see for example the case of $\text{LaSr}_2\text{Fe}_3\text{O}_{12}$.
 - ¹³ T. Saha-Dasgupta, Z. S. Popović, and S. Satpathy, *Phys. Rev. B* **72**, 045143 (2005).
 - ¹⁴ T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, *Phys. Rev. B* **60**, 7309 (1999).
 - ¹⁵ The list is for B -site ordered perovskites where breathing distortions is not due to the spontaneous electron instability, but present because of ordered arrangement of B -site element.
 - ¹⁶ This distortion is not a Jahn-Teller elongation of the octahedra, because the equatorial oxygen of a single octahedron either all elongate (contract) in the same direction; a Jahn-Teller distortion is rather seen as a two-in-two-out distortion of the equatorial oxygen atoms.
 - ¹⁷ G. King and P. M. Woodward, *J. Mater. Chem.* **20**, 5785 (2010).
 - ¹⁸ B. J. Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, *Journal of Applied Crystallography* **39**, 607 (2006).
 - ¹⁹ C. J. Howard and H. T. Stokes, *Acta Crystallographica Section A* **61**, 93 (2005).
 - ²⁰ C. J. Howard and H. T. Stokes, *Acta Crystallographica Section B* **60**, 674 (2004).
 - ²¹ H. T. Stokes, E. H. Kisi, D. M. Hatch, and C. J. Howard, *Acta Crystallographica Section B* **58**, 934 (2002).
 - ²² A. M. Glazer, *Acta Crystallographica Section B* **28**, 3384 (1972).
 - ²³ J. B. Torrance, P. Lacorre, A. I. Nazzari, E. J. Ansaldo, and C. Niedermayer, *Phys. Rev. B* **45**, 8209 (1992).
 - ²⁴ S. J. May, J.-W. Kim, J. M. Rondinelli, E. Karapetrova, N. A. Spaldin, A. Bhattacharya, and P. J. Ryan, *Phys. Rev. B* **82**, 014110 (2010).
 - ²⁵ J. Chakhalian, J. M. Rondinelli, J. Liu, B. A. Gray, M. Kareev, E. J. Moon, N. Prasai, J. L. Cohn, M. Varela, I. C. Tung, M. J. Bedzyk, S. G. Altendorf, F. Strigari, B. Dabrowski, L. H. Tjeng, P. J. Ryan, and J. W. Freeland, *Phys. Rev. Lett.* **107**, 116805 (2011).
 - ²⁶ A. Blanca-Romero and R. Pentcheva, *Phys. Rev. B* **84**, 195450 (2011).
 - ²⁷ A. V. Boris, Y. Matiks, E. Benckiser, A. Frano, P. Popovich, V. Hinkov, P. Wochner, M. Castro-Colin, E. Detemple, V. K. Malik, C. Bernhard, T. Prokscha, A. Suter, Z. Salman, E. Morenzoni, G. Cristiani, H.-U. Habermeyer, and B. Keimer, *Science* **332**, 937 (2011).
 - ²⁸ N. A. Benedek, A. T. Mulder, and C. J. Fennie, *J. Solid State Chem.* **195**, 11 (2012).
 - ²⁹ J.-S. Zhou, J. B. Goodenough, and B. Dabrowski, *Phys. Rev. Lett.* **95**, 127204 (2005).
 - ³⁰ G. Catalan, *Phase Trans.* **81**, 729 (2008).
 - ³¹ J. B. Goodenough, in *Structure and Bonding, Localized to Itinerant Electronic Transitions in Perovskite Oxides*, Vol. 98, edited by J. B. Goodenough (Springer, 2001).
 - ³² J. M. Perez-Mato, D. Orobengoa, and M. I. Aroyo, *Acta Crystallographica Section A* **66**, 558 (2010).
 - ³³ M. T. Dove, *American Mineralogist* **82**, 213 (1997).
 - ³⁴ O. Diéguez, O. E. González-Vázquez, J. C. Wojdeł, and J. Íñiguez, *Phys. Rev. B* **83**, 094105 (2011).
 - ³⁵ R Core Team, *R: A Language and Environment for Statistical Computing*, R Foundation for Statistical Computing, Vienna, Austria (2012), ISBN 3-900051-07-0.
 - ³⁶ D. Sarkar, *Lattice: Multivariate Data Visualization with R* (Springer, New York, 2008) ISBN 978-0-387-75968-5.
 - ³⁷ M. L. Medarde, *Journal of Physics: Condensed Matter* **9**, 1679 (1997).
 - ³⁸ J. A. Alonso, J. L. García-Muñoz, M. T. Fernández-Díaz, M. A. G. Aranda, M. J. Martínez-Lope, and M. T. Casais, *Phys. Rev. Lett.* **82**, 3871 (1999).
 - ³⁹ The first origin choice is only used for notation purposes to avoid confusion. Our actual mode-decomposition was performed using $P2_1/n$ space group as reported in the literature.
 - ⁴⁰ M. Medarde, P. Lacorre, K. Conder, F. Fauth, and A. Furrer, *Phys. Rev. Lett.* **80**, 2397 (1998).
 - ⁴¹ V. I. Anisimov, D. Bukhvalov, and T. M. Rice, *Phys. Rev. B* **59**, 7901 (1999).
 - ⁴² I. I. Mazin, D. I. Khomskii, R. Lengsdorf, J. A. Alonso, W. G. Marshall, R. M. Ibberson, A. Podlesnyak, M. J. Martínez-Lope, and M. M. Abd-Elmeguid, *Phys. Rev. Lett.* **98**, 176406 (2007).
 - ⁴³ J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, J. L. García-Muñoz, and M. T. Fernández-Díaz, *Phys. Rev. B* **61**, 1756 (2000).
 - ⁴⁴ M. Medarde, M. T. Fernández-Díaz, and P. Lacorre, *Phys. Rev. B* **78**, 212101 (2008).
 - ⁴⁵ J. L. García-Muñoz, M. A. G. Aranda, J. A. Alonso, and M. J. Martínez-Lope, *Phys. Rev. B* **79**, 134432 (2009).
 - ⁴⁶ A. Munoz, J. Alonso, M. Martinez-Lope, and M. Fernandez-Diaz, *Journal of Solid State Chemistry* **182**, 1982 (2009).
 - ⁴⁷ A. T. Mulder, N. A. Benedek, J. M. Rondinelli, and C. J. Fennie, ArXiv e-prints (2012), 1205.5526.
 - ⁴⁸ J. Chakhalian, J. M. Rondinelli, J. Liu, B. A. Gray, M. Kareev, E. J. Moon, N. Prasai, J. L. Cohn, M. Varela, I. C. Tung, M. J. Bedzyk, S. G. Altendorf, F. Strigari, B. Dabrowski, L. H. Tjeng, P. J. Ryan, and J. W. Freeland, *Phys. Rev. Lett.* **107**, 116805 (2011).
 - ⁴⁹ J. W. Freeland, J. Liu, M. Kareev, B. Gray, J. W. Kim, P. Ryan, R. Pentcheva, and J. Chakhalian, *EPL (Europhysics Letters)* **96**, 57004 (2011).
 - ⁵⁰ I. C. Tung, P. V. Balachandran, J. Liu, B. A. Gray, E. A. Karapetrova, J. H. Lee, J. Chakhalian, M. J. Bedzyk, J. M. Rondinelli, and J. W. Freeland, Submitted, March (2013).
 - ⁵¹ X. Obradors, L. M. Paulius, M. B. Maple, J. B. Torrance, A. I. Nazzari, J. Fontcuberta, and X. Granados, *Phys. Rev. B* **47**, 12353 (1993).
 - ⁵² I. Vobornik, L. Perfetti, M. Zacchigna, M. Grioni, G. Margaritondo, J. Mesot, M. Medarde, and P. Lacorre, *Phys. Rev. B* **60**, R8426 (1999).
 - ⁵³ S. Lee, R. Chen, and L. Balents, *Phys. Rev. B* **84**, 165119 (2011).
 - ⁵⁴ M. A. Karlow, S. L. Cooper, A. L. Kotz, M. V. Klein, P. D. Han, and D. A. Payne, *Phys. Rev. B* **48**, 6499 (1993).
 - ⁵⁵ M. Braden, W. Reichardt, E. Elkaim, J. P. Lauriat, S. Shiryaev, and S. N. Barilo, *Phys. Rev. B* **62**, 6708 (2000).
 - ⁵⁶ C. Franchini, G. Kresse, and R. Podloucky, *Phys. Rev. Lett.* **102**, 256402 (2009).
 - ⁵⁷ S. Pei, J. D. Jorgensen, B. Dabrowski, D. G. Hinks, D. R. Richards, A. W. Mitchell, J. M. Newsam, S. K. Sinha, D. Vaknin, and A. J. Jacobson, *Phys. Rev. B* **41**, 4126 (1990).
 - ⁵⁸ T. Nishio, J. Ahmad, and H. Uwe, *Phys. Rev. Lett.* **95**, 176403 (2005).